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Bifurcation and merging of wavepackets: Quantum chaos induced by nonadiabatic coupling

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Born–Oppenheimer近似のやぶれをもつ系におけるカオス的なふるまいの原因の1つとして、2つのポテンシャル関数の擬交差付近における振動波束の分岐と融合を考えることができる。ここではそのような波束の挙動の直接観測を目的としたNaI分子における分子振動ダイナミクスのフェムト秒光電子分光を量子波束計算で示し、あわせてこのような系に有効なカオスの強さを計る指標を適用する。

Introduction: Molecular systems exhibiting nonadiabaticity due to breakdown of Born–Oppenheimer approximation has been known to show "chaotic" spectra. It is recently recognized (from statistical arguments) that nonadiabatic interaction itself can be the cause of apparent chaos [1], suggesting a class of chaos that has no classical counterpart. To further investigate the *dynamical* aspects of the problem, two "measures" of chaos, D_0 and D_3, computed only from wavepacket dynamics were proposed [2]. The NaI molecule is a prototypical nonadiabatic system with a crossing between an ionic and covalent curve in the diabatic representation. We theoretically show how its vibrational wavepacket dynamics can be tracked in real time through femtosecond photoelectron spectroscopy, with a view towards studying quantum chaos.

Formulation: The measure of chaos D_0 is defined in [2] as the difference of density operators made partly decoherent by a subdivision of configuration space. D_3 is a formulation of Hilbert space distance between two wave functions made decoherent in the same manner.

To compute the femtosecond photoelectron spectra, the system is expanded on the two diabatic neutral and the final ion electronic states. A coupled quantum equation of motion for the nuclear wave function corresponding to the three states are integrated using the standard split-operator propagator and Fourier grid methods. All necessary interaction matrix elements between the states due to pump–probe pulses are computed and included as well as a modeling of the intrinsic nonadiabatic interaction [3].

Numerical Results: The computed wave functions are shown in the left panels of Figs. 1(a) and (b) as squared amplitudes at selected times, overlayed on the associated potential curves V_1 (solid) and V_2 (dashed). In Fig. 1(a), the wavepacket on V_1 approaches the avoided crossing from the right, where the wavepacket bifurcates into components on both potential curves resulting in two different vibrational frequencies. Due to the steep slope of V_1 and relative flatness of V_2, the wavepackets are clearly reflected in the photoelectron signals (right panels) enabling us to track the real-time motion. Wavepacket on V_2 appears as photoelectron signal near 0.5 eV, with that on V_1 giving rise to signal moving from a higher to lower energy as the wavepacket moves downhill. Figure 1(b) similarly shows the two components in Fig. 1(a) joining back to form a single wave function on the V_1 curve.

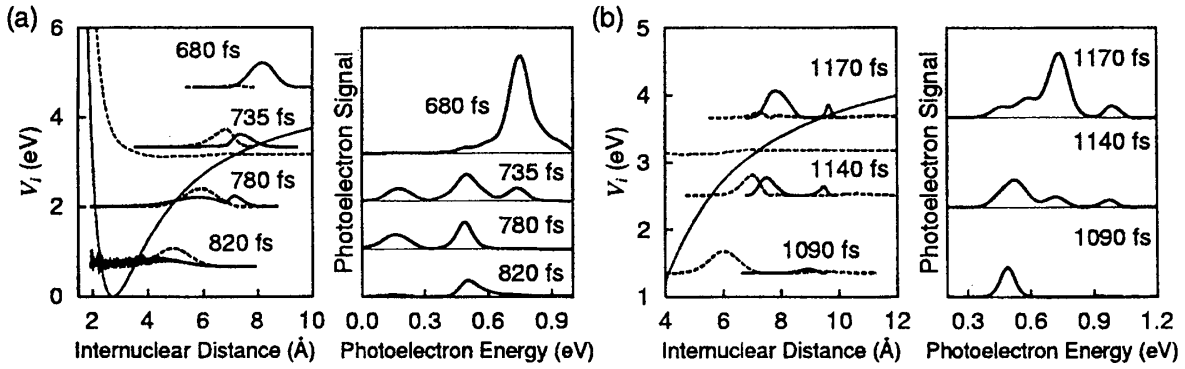

Fig. 1: Wave function snapshots and corresponding photoelectron spectra at selected time delays near occurrence of (a) wavepacket bifurcation and (b) wavepacket merging.

Measures of chaos D_0 and D_3 for the system are presented in Figs. 2(a) and (b) respectively, along with curves (labeled adiabatic) computed neglecting nonadiabatic interaction. The curves show steep initial decrease indicative of chaos. In the calculation including nonadiabatic effects, the curves also show a steady decrease with time due to dissociation of the molecule.

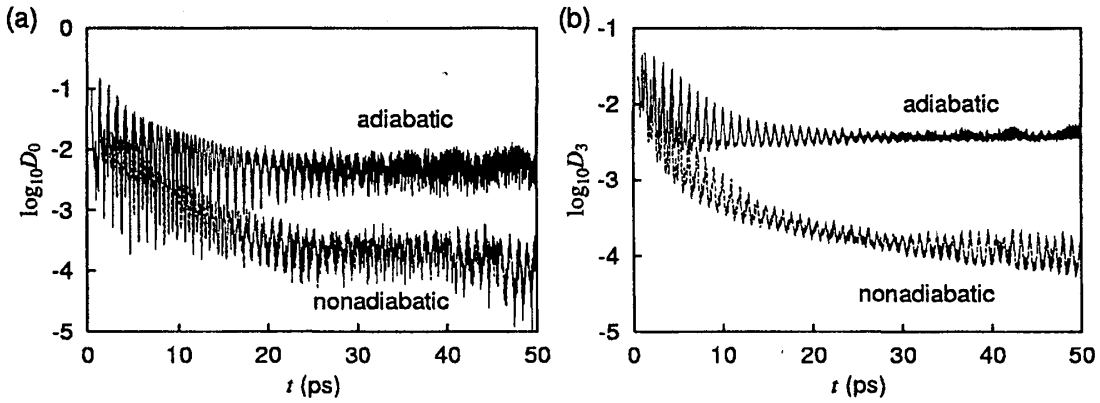

Fig. 2: Long time (a) D_0 and (b) D_3 behavior for the NaI system.

Conclusions: We have shown a molecular system where nonadiabatic dynamics featuring wavepacket bifurcating/merging can directly be observed. Experimental as well as theoretical investigation of wavepacket dynamics in this and other nonadiabatic systems should provide further insight into a kind of purely quantum chaos and warrants further study.

[1] H. Fujisaki and K. Takatsuka, Phys. Rev. E **63**, 066221 (2001).

[2] H. Higuchi and K. Takatsuka, Phys. Rev. E **66**, 035203 (2002); K. Takatsuka, Bussei Kenkyu (Kyoto) **82**, 715 (2004).

[3] Y. Arasaki, K. Takatsuka, K. Wang, and V. McKoy, Phys. Rev. Lett. **90**, 248303 (2003); J. Chem. Phys. **119**, 7913 (2003).